

# Electron spin resonance shifts in $S = 1$ antiferromagnetic chains

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We discuss electron spin resonance (ESR) shifts in spin-1 Heisenberg antiferromagnetic chains with a weak single-ion anisotropy based on several effective field theories, the  $O(3)$  nonlinear sigma model (NLSM) in the Haldane phase, free fermion theories around the lower and the upper critical fields. In the  $O(3)$  NLSM, the single-ion anisotropy corresponds to a composite operator which creates two magnons at the same time and position. Therefore, even inside a parameter range where free magnon approximation is valid, we have to take interactions among magnons into account. Though the  $O(3)$  NLSM is only valid in the Haldane phase, an appropriate translation of Faddeev-Zamolodchikov operators of the  $O(3)$  NLSM to fermion operators enables one to treat ESR shifts near the lower critical field in a similar manner to discussions in Haldane phase. We present that our theory gives quantitative agreements with recent ESR experimental results on an spin-1 chain compounds NDMAP.

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## I. INTRODUCTION

Quantum phase transition has been studied for a long time. In quantum magnetism, the magnetic field is the most familiar parameter to cause quantum phase transitions. An  $S = 1$  Heisenberg antiferromagnetic (HAF) chain and an  $S = 1/2$  two-leg HAF ladder are typical examples of one-dimensional quantum spin systems which show the quantum phase transition by the magnetic field. These systems have the unique ground state separated from excited states by a finite excitation gap at zero field. As the magnetic field is gradually applied, the excitation gap is going to vanish.<sup>1,2</sup> After the collapse of the excitation gap, the system enters into a field-induced critical phase. The field-induced critical phase lies in a range  $H_{c1} < H < H_{c2}$ . Here  $H_{c1}$  and  $H_{c2}$  are called as a lower and an upper critical field. For  $H < H_{c1}$ , the system is in the gapped phase. And for  $H_{c2} < H$ , the system is in another gapped phase where the spins are fully polarized.  $H_{c2}$  is also called as a saturation field.

The quantum phase transitions at  $H = H_{c1}$  and  $H = H_{c2}$  bring about reconstructions of the excitation spectrum. Especially, dynamical properties of low-energy excitations are dramatically changed. Recently, dynamics of electron spins in the field-induced critical phases are actively investigated by various experimental techniques.<sup>3-5</sup> Among these experimental techniques, electron spin resonance (ESR) occupies a unique position in its sensitivity to interactions between electron spins. In fact, thanks to this advantage of ESR, many interesting ESR experiments have been performed in one-dimensional quantum spin systems under high magnetic field.<sup>4-6</sup> These recent precise ESR experiments enhance the significance of reliable quantitative theory of ESR in the field-induced critical phase.

Despite the theoretical and experimental importance of the field-induced critical phase, ESR in the field-induced

critical phase is less studied by theorists. This situation is in contrast to the fact that  $S = 1/2$  HAF critical chain whose low-temperature ESR is well understood.<sup>7-10</sup> Note that ESR of the  $S = 1$  HAF chain has been well studied.<sup>11,12</sup> However, these theories mainly treat the gapped phase of  $S = 1$  HAF chains. Thus, it is an objective of the present paper to propose a theory of ESR in the field-induced critical phase, especially around quantum critical points, of one-dimensional quantum spin systems in an organized manner.

In this paper, we consider an  $S = 1$  HAF chain with a general form of a single-ion anisotropy

$$\mathcal{H} = J \sum_j \mathbf{S}_j \cdot \mathbf{S}_{j+1} - g_e \mu_B H \sum_j S_j^z + D \sum_j (S_j^p)^2 + E \sum_j [(S_j^q)^2 - (S_j^r)^2] \quad (1)$$

in the whole range of the magnetic field, from zero field  $H = 0$  to the saturation field  $H = H_{c2}$ .  $g_e$  and  $\mu_B$  are Landé  $g$  factor of electron spin and  $\mu_B$  is Bohr magneton. We put  $\hbar = k_B = g_e \mu_B = 1$  unless otherwise stated. Especially we focus on a shift of the resonance frequency (ESR shift) caused by weakly anisotropic spin-spin interactions.

We reported, in our preceding Rapid Communication,<sup>13</sup> that the ESR shift in a range  $H \lesssim H_{c1}$  is well explained by, so called, the form factor perturbation theory<sup>14</sup> (FFPT) around an integrable field theory. In the case of  $S = 1$  HAF chain, the  $O(3)$  nonlinear sigma model (NLSM) plays the role of the unperturbed integrable field theory in FFPT. In the Rapid Communication,<sup>13</sup> we applied the FFPT to the analysis of the ESR shift in  $H \approx 0$  and  $H \approx H_{c1}$ , where we utilized a close relation of effective field theories in two different regions,  $H \approx 0$  and  $H \approx H_{c1}$ . This paper is also intended to take a closer look at this remarkable feature.

In the next section, we will briefly review a general framework of perturbative treatments for the ESR shift. We consider ESR shifts in three regions; the low-field gapped region (Sec. IV); a region near the lower critical field (Sec. V); and a region near the upper critical field (Sec. VI). In each region, we introduce an effective field theory and apply it to analysis of the ESR shift at low temperature. Sec. VII is devoted to a comparison of our theory with recent ESR experiments<sup>5</sup> of an  $S = 1$  HAF compound. In App. A, we discuss a qualitative difference of the single-ion anisotropy and an exchange anisotropy from the viewpoint of ESR shifts.

## II. FRAMEWORK

Here we briefly review the perturbation theory of the ESR shift. The ESR experiments measure an absorption of an oscillating magnetic field by electron spins, where a microwave is typically applied. From the absorption spectrum, we are able to extract information on dynamics of electron spins. Within the linear response theory, the ESR spectrum  $I(\omega) \propto \omega \chi''_{+-}(\omega, q)$  is written in the retarded Green's function,

$$\chi''_{+-}(\omega, q = 0) = \text{Im} \left[ i \int_0^\infty dt e^{i\omega t} \langle [S^+(t), S^-(0)] \rangle \right]. \quad (2)$$

Here  $S^\pm = S^x \pm iS^y$  denote transverse components of the total spin  $\mathbf{S} = \sum_j \mathbf{S}_j$ . The correlation  $\langle [S^+(t), S^-(0)] \rangle$  is SU(2) invariant. Thus, if the whole Hamiltonian preserves the SU(2) symmetry in the spin space, (2) is trivially constant. In the presence of the magnetic field, the symmetry of the Hamiltonian is lowered to U(1) at most. If spin-spin interactions preserve the SU(2) symmetry, (2) is simple despite the presence of interactions.

$$\chi''_{+-}(\omega, q = 0) = 2\pi \langle S^z \rangle \delta(\omega - H). \quad (3)$$

The resonance frequency  $\omega_r$  equals to the paramagnetic one  $\omega_r = H$  at any temperature.

If spin-spin interactions do not preserve the SU(2) symmetry, the above discussion breaks down and the resonance frequency is shifted from the paramagnetic one. Let us assume that the Hamiltonian is composed of three terms,

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_Z + \mathcal{H}', \quad (4)$$

where  $\mathcal{H}_0$  represents SU(2) symmetric interactions,  $\mathcal{H}_Z$  is the Zeeman term, and  $\mathcal{H}'$  represents anisotropic interactions. The model (1) has the same form as (4). If the anisotropic interaction is weak, we are able to consider a perturbative expansion of the resonance frequency.

The first order perturbative expansion of the resonance frequency was proposed first by Kanamori and Tachiki<sup>15</sup> and later applied to quantum spin systems by Nagata and Tazuke.<sup>10,16,17</sup> Ref. 18 derived the ESR shift  $\delta\omega =$

$\omega_r - H$  from equal-time correlations at the lowest order in a general formalism,

$$\delta\omega = -\frac{\langle [[\mathcal{H}', S^+], S^-] \rangle_0}{2\langle S^z \rangle_0} + \dots \quad (5)$$

The average  $\langle \dots \rangle_0$  is taken with respect to the unperturbed Hamiltonian  $\mathcal{H}^{(0)}$ ,

$$\mathcal{H}^{(0)} = \mathcal{H}_0 + \mathcal{H}_Z. \quad (6)$$

While we thus far treated the ESR spectrum as a function of the frequency  $\omega$  with a fixed  $H$  in above discussions, this is often not the case in actual ESR experiments. The ESR spectrum is usually obtained as a function of  $H$  with a fixed  $\omega$ . In this case, the ESR shift is defined as

$$\delta H = H_r - \omega / g_e \mu_B. \quad (7)$$

$H_r$  is the resonance field. Note that the  $g$  factor used in (7) is determined at the high temperature limit. By definition, (7) approaches zero as  $T \rightarrow +\infty$ . At a low temperature  $T \lesssim J$ , it generally holds that  $\delta H \neq 0$ . According to Refs. 8 and 9, within the first order accuracy, the ESR shift (7) satisfies

$$g_e \mu_B \delta H = \frac{\langle [[\mathcal{H}', S^+], S^-] \rangle_0}{2\langle S^z \rangle_0}. \quad (8)$$

We should emphasize that Eq. (8) is equivalent to (5). Therefore, as long as we are concerned with the first order perturbation theory around (6), it does not matter whether we change  $\omega$  or  $H$ .

We apply the formula (5) to our model (1), namely,

$$\mathcal{H}^{(0)} = J \sum_j \mathbf{S}_j \cdot \mathbf{S}_{j+1} - \sum_j \mathbf{H} \cdot \mathbf{S}_j, \quad (9)$$

$$\mathcal{H}' = D \sum_j (S_j^p)^2 + E \sum_j [(S_j^q)^2 - (S_j^r)^2]. \quad (10)$$

The ESR shift (5) is, in this case, given by

$$\delta\omega = f_D(\mathbf{z}) Y_D(T, H), \quad (11)$$

$$f_D(\mathbf{z}) = D(1 - 3z_p^2) - 3E(z_q^2 - z_r^2), \quad (12)$$

$$Y_D(T, H) = \frac{1}{2\langle S^z \rangle_0} \sum_j [3\langle (S_j^z)^2 \rangle_0 - 2] \quad (13)$$

The unit vector  $\mathbf{z} \equiv \mathbf{H}/H$  is parallel to the magnetic field. And  $\mathbf{z} = (z_p, z_q, z_r)$  is represented in the  $(p, q, r)$  coordinate in (1). Thus, if we fix the orientation of the magnetic field, then we may regard  $f_D(\mathbf{z})$  as a constant. For simplicity, we hereafter set  $\mathbf{H} = H\hat{z}$  where  $\hat{z}$  is the unit vector along  $z$  axis. We call  $Y_D(T, H)$  as a normalized ESR shift. The normalized ESR shift is useful for our purpose because it can be applied to systems with any value of  $D$  and  $E$ .

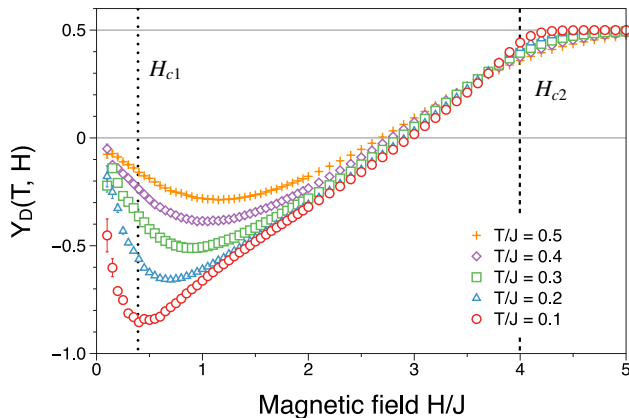


Figure 1. (Color online) Quantum Monte Carlo results of the normalized ESR shift (13) induced by the single-ion anisotropy (10) for temperatures  $T/J = 0.1 - 0.5$ . The system size is  $L = 40$  sites. The lower critical field  $H_{c1} = 0.41J$  and the upper critical field  $H_{c2} = 4J$  are guided by the dotted and the dashed lines respectively. There is an extremum around  $H = H_{c1} + T$ . This non-monotonic behaviour of the ESR shift is understood by the finite temperature crossover.

### III. QMC RESULTS

We numerically derived the normalized ESR shift (13) from quantum Monte Carlo (QMC) calculations. The QMC results of the  $H$  dependence of  $Y_D(T, H)$  is shown in Fig. 1. We found several characteristics from Fig. 1. (i) The normalized shift is approximately proportional to  $H$  in the ranges  $0 < H < H_{c1}$  and  $H_{c1} < H < H_{c2}$ . The slope  $\partial_H Y_D(T, H)$  is negative in the former and positive in the latter range. (ii) The normalized shift has a minimum around  $H = H_{c1}$ . The field which gives the minimum increases as the temperature increases. (iii) The normalized shift becomes zero at a certain value of  $H$  because  $Y_D(T, H = 0) = 0$  and  $\partial_H Y_D(T, H)|_{H=0} < 0$  hold at  $H = 0$  and the saturating value  $Y_D(T, H > H_{c2})$  is positive. Note that the field dependence in Fig. 1 is qualitatively different from that of  $S = 1/2$  HAF two-leg ladder systems.<sup>19</sup> In  $S = 1/2$  HAF two-leg ladder systems, we fail to find the change of the sign of the ESR shift. Namely, the normalized shift is non-zero from the infinitely weak field to the saturation field (see Fig.1 in Ref. 19). The above three features suggest that the magnetic field dependence of the normalized ESR shift reflects the finite-temperature crossover. Below we analyze the normalized shift (13) in the gapped, lower critical, upper critical regions.

## IV. LOW-FIELD GAPPED PHASE

### A. Effective field theory

First we review the zero-field case, then we will extend the argument to the low-field case. The unperturbed model (6) in the absence of the magnetic field,

$$\mathcal{H}_0 = J \sum_j \mathbf{S}_j \cdot \mathbf{S}_{j+1}. \quad (14)$$

has an excitation gap  $\Delta_0 = 0.41J$ ,<sup>20</sup> which is called as the Haldane gap. Haldane proposed that HAF chains with an integer quantum spin number  $S$  have an excitation gap  $\Delta_0$  based on a semiclassical field theory, the  $O(3)$  nonlinear sigma model (NLSM).<sup>21,22</sup> The  $O(3)$  NLSM has a Lagrangian,

$$\mathcal{L} = \frac{1}{2g} \partial_\mu \mathbf{n} \cdot \partial^\mu \mathbf{n} + \frac{\Theta}{4\pi} \mathbf{n} \cdot \partial_t \mathbf{n} \times \partial_x \mathbf{n}. \quad (15)$$

The contraction  $\partial_\mu \mathbf{n} \cdot \partial^\mu \mathbf{n} = (\partial_t \mathbf{n})^2 - (\partial_x \mathbf{n})^2$  was taken. For simplicity we put the spin-wave velocity to unity. The field  $\mathbf{n}(t, x)$  represents an antiferromagnetic order:

$$\mathbf{S}_x \sim \sqrt{S(S+1)}(-1)^x \mathbf{n}(x) + \mathbf{L}(x) \quad (16)$$

The uniform component  $\mathbf{L} = \mathbf{n} \times \partial_t \mathbf{n}/g$  is quadratic in  $\mathbf{n}$ . The coupling constant  $\Theta = 2\pi S$  is equal to 0 or  $\pi$  mod  $2\pi$ .

The  $O(3)$  NLSM is integrable when  $\Theta \equiv 0, \pi$  (mod  $2\pi$ ). In the case  $\Theta \equiv \pi$ , the  $O(3)$  NLSM is critical.<sup>23</sup> On the other hand, in the case  $\Theta \equiv 0$  of our interest, the  $O(3)$  NLSM has massive triplet particles, which is called magnons, as the lowest excitations. The triplet magnons are created by  $n^a(t, x) \propto (-1)^x S^a(t, x)$  ( $a = x, y, z$ ). Thus, the field  $S^a$  satisfies the relation

$$(-1)^x \langle 0 | S^a(t, x) | \theta_1, a_1 \rangle = \delta_{aa_1} \sqrt{Z} e^{ix^\mu p_\mu}. \quad (17)$$

$|0\rangle$  is the ground state,  $|\theta_1, a_1\rangle$  is a one-magnon state with the rapidity  $\theta_1$  and the index  $a_1 = x, y, z$ , and  $Z$  is the renormalization factor which will be discussed later. The  $O(3)$  NLSM is Lorentz invariant, and the triplet excitations obey a dispersion relation  $p_0 = \sqrt{\Delta_0^2 + p_1^2}$  parametrized by a single parameter  $\theta$ .

$$p_0 = \Delta_0 \cosh \theta, \quad p_1 = \Delta_0 \sinh \theta \quad (18)$$

This parameter  $\theta$  is called as a rapidity, which uniquely determines the energy  $p_0$  and the momentum  $p_1$  of magnons. Therefore, the one-magnon state  $|\theta_1, a_1\rangle$  is fully characterized by the rapidity  $\theta_1$  and the index  $a_1$ . We normalize the state  $|\theta, a\rangle$  by

$$\langle \theta_1, a_1 | \theta_2, a_2 \rangle = 4\pi \delta_{a_1 a_2} \delta(\theta_1 - \theta_2). \quad (19)$$

Instead of the one-magnon state, we may consider creation and annihilation operators of magnons, which we

denote  $Z_a(\theta)$  and  $Z_a^\dagger(\theta)$  respectively. These  $Z_a(\theta)$  and  $Z_a^\dagger(\theta)$  are called as Faddeev-Zamolodchikov (FZ) operators and satisfy the following algebra.

$$Z_{a_1}(\theta_1)Z_{a_2}(\theta_2) = S_{a_1 a_2}^{b_1 b_2}(\theta_1 - \theta_2)Z_{b_2}(\theta_2)Z_{b_1}(\theta_1) \quad (20)$$

$$Z_{a_1}^\dagger(\theta_1)Z_{a_2}^\dagger(\theta_2) = S_{a_1 a_2}^{b_1 b_2}(\theta_1 - \theta_2)Z_{b_2}^\dagger(\theta_2)Z_{b_1}^\dagger(\theta_1) \quad (21)$$

$$\begin{aligned} Z_{a_1}(\theta_1)Z_{a_2}^\dagger(\theta_2) &= 4\pi\delta_{a_1 a_2}\delta(\theta_1 - \theta_2) \\ &\quad + S_{a_2 b_1}^{b_2 a_1}(\theta_1 - \theta_2)Z_{b_2}^\dagger(\theta_2)Z_{b_1}(\theta_1) \end{aligned} \quad (22)$$

The factor  $S_{ab}^{cd}(\theta)$  is an  $S$  matrix. The  $S$  matrix possesses information of two-magnon scatterings. If the magnon created by  $Z_a^\dagger(\theta)$  were a free boson (a free fermion), the  $S$  matrix is simply  $S_{ab}^{cd}(\theta) = \delta_{ad}\delta_{bc}$  ( $S_{ab}^{cd}(\theta) = -\delta_{ad}\delta_{bc}$ ). In reality, the magnon is neither boson nor fermion. Thus, the  $S$  matrix is complicated and it depends on the rapidity. Fortunately  $S$  matrix of the O(3) NLSM is exactly known.

$$S_{ab}^{cd}(\theta) = \delta_{ab}\delta_{cd}\sigma_1(\theta) + \delta_{ac}\delta_{bd}\sigma_2(\theta) + \delta_{ad}\delta_{bc}\sigma_3(\theta) \quad (23)$$

$\sigma_i(\theta)$ 's ( $i = 1, 2, 3$ ) are

$$\begin{aligned} \sigma_1(\theta) &= \frac{2\pi i\theta}{(\theta + \pi i)(\theta - 2\pi i)}, \\ \sigma_2(\theta) &= \frac{\theta(\theta - \pi i)}{(\theta + \pi i)(\theta - 2\pi i)}, \\ \sigma_3(\theta) &= \frac{2\pi i(\pi i - \theta)}{(\theta + \pi i)(\theta - 2\pi i)}. \end{aligned}$$

Using the FZ operator, we can create a one-magnon state  $|\theta, a\rangle$  and its conjugate,

$$|\theta, a\rangle = Z_a^\dagger(\theta)|0\rangle, \quad \langle\theta, a| = \langle 0|Z_a(\theta). \quad (24)$$

$n$ -magnon states are specified by a set of rapidities  $\{\theta_1, \dots, \theta_n\}$  and indices  $\{a_1, \dots, a_n\}$ , that is,

$$\begin{aligned} |\theta_1, a_1; \dots; \theta_n, a_n\rangle &= Z_{a_1}^\dagger(\theta_1) \dots Z_{a_n}^\dagger(\theta_n)|0\rangle, \\ \langle\theta_1, a_1; \dots; \theta_n, a_n| &= \langle 0|Z_{a_n}(\theta_n) \dots Z_{a_1}(\theta_1). \end{aligned}$$

They are normalized as follows:

$$\begin{aligned} \langle\theta_1, a_1; \dots; \theta_n, a_n|\theta'_1, a'_1; \dots; \theta'_n, a'_n\rangle \\ = \delta_{nm}(4\pi)^n \prod_{l=1}^n \delta_{a_l a'_l} \delta(\theta_l - \theta'_l) \end{aligned} \quad (25)$$

A matrix element

$$F_{\mathcal{O}}(\theta_1, a_1; \dots; \theta_n, a_n) = \langle 0|\mathcal{O}(0)|\theta_1, a_1; \dots; \theta_n, a_n\rangle \quad (26)$$

is called as an  $n$ -magnon form factor of a local operator  $\mathcal{O}(t, x)$ . Here  $\mathcal{O}(0)$  is an abbreviation of  $\mathcal{O}(0, 0)$ . A Lorentz boost of the O(3) NLSM alters (26) to

$$\begin{aligned} \langle 0|\mathcal{O}(t, x)|\theta_1, a_1; \dots; \theta_n, a_n\rangle \\ = F_{\mathcal{O}}(\theta_1, a_1; \dots; \theta_n, a_n)e^{i(tP_0 - xP_1)}, \end{aligned} \quad (27)$$

where  $P_0$  and  $P_1$  denote the total energy and momentum.

$$P_0 = \sum_{m=1}^n \Delta_0 \cosh \theta_m, \quad P_1 = \sum_{m=1}^n \Delta_0 \sinh \theta_m. \quad (28)$$

For example, the relation (17) is equivalent to the one-magnon form factor of  $S^a$  at the origin

$$F_{S^a}(\theta_1, a_1) = (-1)^r \sqrt{Z} \delta_{a, a_1}. \quad (29)$$

The relation (17) connects the low-energy effective field theory and the physical operator  $S^a(t, x)$  in the original spin model. The renormalization factor  $\sqrt{Z}$  inevitably depends on short-distance, non-universal physics and cannot be determined within the effective field theory.  $Z$  is determined only by numerical calculations.  $Z \approx 1.26$  is concluded from Density matrix renormalization group calculations.<sup>24,25</sup> It is emphasized that eq. (29) should *not* be interpreted as an identity between the physical spin operator  $S^a$  and the FZ operator. The spin operator  $S^a$  also has nonvanishing higher-order form factors. Thus the form factor of the powers of  $S^a$  is not solely determined by the one magnon form factor (29), even in the leading order.

Let us consider the traceless symmetric tensor

$$\Sigma^{ab} \equiv S^a S^b - \frac{2}{3} \delta_{ab}. \quad (30)$$

$\Sigma^{ab}$  has a two-magnon form factor,

$$F_{\Sigma^{ab}}(\theta_1, a_1; \theta_2, a_2) = -iZ_2 \delta_{ab} \delta_{a_1 a_2} (3\delta_{aa_1} - 1) \psi_2(\theta_1 - \theta_2). \quad (31)$$

In the case of O( $N$ ) NLSM,<sup>26</sup>  $\psi_2(\theta)$  is given by an integral.

$$\psi_2(\theta) = \sinh\left(\frac{\theta}{2}\right) \exp\left[\int_0^\infty \frac{dx}{x} K_N(x) \frac{\cosh[(\pi + i\theta)x] - 1}{\sinh(\pi x)}\right] \quad (32)$$

$$K_N(x) = \frac{e^{-\pi x} + e^{-2\pi x/(N-2)}}{1 + e^{-\pi x}} \quad (33)$$

We performed the integral and derived an explicit form of  $\psi_2(\theta)$  for the  $N = 3$  case in our preceding paper.<sup>13</sup>

$$\psi_2(\theta) = \frac{i}{2}(\theta - \pi i) \tanh\left(\frac{\theta}{2}\right) \quad (34)$$

The two-magnon form factor (31) is now determined except for the non-universal factor  $Z_2$ . We emphasize that  $Z_2$  is an independent parameter from  $Z$ . We have determined  $Z_2 \approx 0.24$  by using the infinite time evolving block decimation method.<sup>13</sup>

The basis  $\{|\theta_1, a; \dots; \theta_n, a_n\rangle\}$  with  $n = 0, 1, 2, \dots$  is complete and orthonormal. The identity  $\hat{1}$  reads

$$\begin{aligned} \hat{1} &= |0\rangle\langle 0| + \sum_{n=1}^\infty \frac{1}{n!} \sum_{a_1 \dots a_n} \int_{-\infty}^\infty \frac{d\theta_1 \dots d\theta_n}{(4\pi)^n} \\ &\quad \times |\theta_1, a_1; \dots; \theta_n, a_n\rangle\langle\theta_1, a_1; \dots; \theta_n, a_n|. \end{aligned} \quad (35)$$

We note that an important relation of form factors, the crossing relation. In subsequent sections, we will encounter matrix elements such as  $\langle \theta_2, a_2 | \mathcal{O}(0) | \theta_1, a_1 \rangle$ . The crossing relation allows one to relate this matrix element to form factors.

$$\begin{aligned} \langle \theta_2, a_2 | \mathcal{O}(0) | \theta_1, a_1 \rangle &= \langle 0 | \mathcal{O}(0) | \theta_1, a_1; \theta_2 - \pi i, \bar{a}_2 \rangle \\ &= F_{\mathcal{O}}(\theta_1, a_1; \theta_2 - \pi i, \bar{a}_2) \end{aligned} \quad (36)$$

The index  $\bar{a}$  represents an index of an anti-magnon conjugate to the magnon with the index  $a$ . If we employ the labeling  $a = x, y, z$ , then  $\bar{a} = a$  holds. If, on the other hand, we employ a labeling  $a = +, 0, -$ , namely  $(n^+, n^0, n^-) = ((n^x + in^y)/\sqrt{2}, n^z, (n^x - in^y)/\sqrt{2})$ , we have  $\bar{+} = -$ ,  $\bar{0} = 0$  and  $\bar{-} = +$ . The latter labeling is required in the presence of a weak magnetic field.

Under a weak magnetic field  $H < \Delta_0$ , the unperturbed system (9) still have a finite gap  $\Delta_0 - H$ . Here we have to replace the dispersion relation (18) to

$$p_0 = \Delta_0 \cosh \theta - aH, \quad p_1 = \Delta_0 \sinh \theta, \quad (37)$$

where  $a = 0, +, -$ . Thus, the triplet degeneracy is lifted by the Zeeman splitting term. If the magnetic field is very weak  $H \ll \Delta_0$ , then we may use the form factors evaluated for the  $H = 0$  case at the lowest order of  $H$ .

### B. ESR shift

In the limit  $H, T \rightarrow 0$ , the density of magnons becomes low. It should be reasonable in this dilute limit that we ignore multi-magnon contributions to, for instance, the magnetization and the normalized shift (13). We multiply a projection operator

$$P_1 = \sum_{a=0,+,-} \int_{-\infty}^{\infty} \frac{d\theta}{4\pi} |\theta, a\rangle \langle \theta, a|$$

to an operator  $\mathcal{O}$  so that the multi-magnon contributions to the average  $\langle \mathcal{O} \rangle$  are projected out. Let us consider  $\mathcal{O} = \Sigma^{00}(0, x)$ . Using the crossing relation (36) and the two-magnon form factor (31), we obtain

$$\begin{aligned} P_1 \Sigma^{00}(0, x) P_1 &= -iZ_2 \int_{-\infty}^{\infty} \frac{d\theta d\theta'}{(4\pi)^2} \psi_2(\theta' - \theta + \pi i) e^{ix[P_1(\theta') - P_1(\theta)]} \\ &\quad \times (2|\theta, 0\rangle \langle \theta, 0| - |\theta, +\rangle \langle \theta', +| - |\theta, -\rangle \langle \theta', -|). \end{aligned} \quad (38)$$

Thus, in the dilute limit, the numerator  $\sum_j [3\langle (S_j^z)^2 \rangle_0 - 2]$  of the normalized shift (13) is approximated as follows.

$$\begin{aligned} &\sum_j [3\langle (S_j^z)^2 \rangle_0 - 2] \\ &= 3 \int dx \langle \Sigma^{00}(0, x) \rangle_0 \\ &\sim -6Z_2 \int_{-\infty}^{\infty} \frac{vd\theta}{4\pi E(\theta)} e^{-E(\theta)/T} \sinh^2\left(\frac{H}{2T}\right) \end{aligned} \quad (39)$$

Here  $E(\theta) = \Delta_0 \cosh \theta$  is the zero-field dispersion. Similarly, the magnetization is given by

$$\langle S^z \rangle_0 \sim 2 \sinh\left(\frac{H}{T}\right) \int_{-\infty}^{\infty} \frac{d\theta}{4\pi} e^{-E(\theta)/T}. \quad (40)$$

From (39) and (40), the normalized shift in the dilute limit reads

$$Y_D(T, H) = -\frac{3Z_2}{4} \tanh\left(\frac{H}{2T}\right) \frac{\int_{-\infty}^{\infty} \frac{vd\theta}{4\pi E(\theta)} e^{-E(\theta)/T}}{\int_{-\infty}^{\infty} \frac{d\theta}{4\pi} e^{-E(\theta)/T}}. \quad (41)$$

(41) correctly reproduces the features of the normalized shift,  $Y_D(T, H) \propto H$  and  $\partial_H Y_D(T, H) < 0$  in the limit  $H \rightarrow 0$ . However, (41) cannot explain the upturn of the normalized shift around  $H = H_{c1}$ . In order to extend (41) to the region  $H \sim H_{c1}$ , we must take into account the repulsive interaction between magnons.

## V. NEAR LOWER CRITICAL FIELD

### A. Effective field theory

At  $H = \Delta_0$ , the lowest magnon band specified by the index  $a = +$  touches the ground state. The point  $H_{c1} \equiv \Delta_0$  corresponds to a quantum critical point. Above  $H_{c1}$ , gapless excitations exist. Thus,  $H = H_{c1}$  separates the low-field gapped phase (called as the Haldane phase) and the high-field gapless phase (the field induced critical phase). We call  $H_{c1}$  the lower critical field. The quantum phase transition occurs only at  $T = 0$ . At finite temperature, there is a region which reflects features of the quantum critical point. This region is usually called as a quantum critical region, which is characterized by  $|H - H_{c1}| \lesssim T$ .

It is known that a free fermion theory describes low-energy behavior of  $S = 1$  HAF chain in the quantum critical region.<sup>1,27-30</sup> The free fermion has a dispersion relation,

$$E(k) = \frac{k^2}{2\Delta_0} - \mu. \quad (42)$$

The chemical potential is  $\mu = H - H_{c1}$ . As the chemical potential of the free fermion increases, the number of the free fermion also increases. In terms of spin systems, the number of the free fermion is identical to the magnetization density  $m_+(T, H) \equiv \langle S^z \rangle_0 / L$ .

$$\begin{aligned} m_+(T, H) &= \sqrt{\frac{\Delta_0}{2\pi^2}} \int_0^{\infty} d\epsilon D(\epsilon) f(\epsilon - \mu) \\ &= -\sqrt{\frac{T\Delta_0}{2\pi}} \text{Li}_{1/2}(-e^{\mu/T}) \end{aligned} \quad (43)$$

$L$  is the length of the spin chain,  $D(\epsilon) = \epsilon^{-1/2}$  is the density of states, and  $f(\xi) = (e^{\xi/T} + 1)^{-1}$  is the Fermi



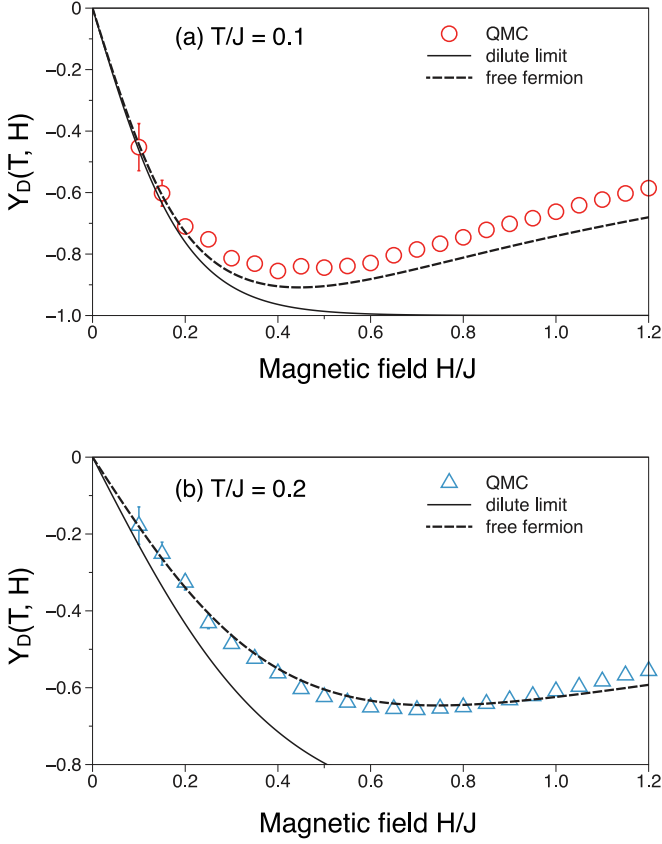


Figure 2. (Color online) Comparisons of QMC and analytic results at (a)  $T/J = 0.1$  and at (b)  $T/J = 0.2$ . Open symbols (circles and triangles) represents QMC data. The solid curves denote the normalized shift in the dilute limit (41). The dashed curves correspond to (47).

distribution function. In the second line, the integral is performed explicitly, with the result given in terms of the polylogarithm function

$$\text{Li}_n(x) = \sum_{m=1}^{\infty} \frac{x^m}{m^n}. \quad (44)$$

Above the quantum critical region  $H \gtrsim H_{c1}$ , a gapless excitation with a linear dispersion  $E(k) \sim k$  dominates the low-temperature physics of the  $S = 1$  HAF chain. The excitation is identified with the Tomonaga-Luttinger (TL) liquid.<sup>2,31</sup> We do not go into detail on the TL liquid in the field-induced critical phase.

## B. ESR shift

Since  $\{|\theta_1, a_1; \dots; \theta_n, a_n\rangle\}$  is complete, we can expand the arbitrary operator  $\mathcal{O}(t, x)$  in the power of FZ opera-

tors. For instance,  $\int dx \Sigma^{aa}(0, x)$  is expanded as

$$\begin{aligned} & \int dx \Sigma^{aa}(0, x) \\ &= \frac{Z_2}{2} \int_{-\infty}^{\infty} \frac{v d\theta}{4\pi E(\theta)} [2Z_0^\dagger(\theta)Z_0(\theta) - Z_+^\dagger(\theta)Z_+(\theta) \\ & \quad - Z_-^\dagger(\theta)Z_-(\theta)] + (\text{higher-order terms}). \end{aligned} \quad (45)$$

The omitted higher-order terms contain, for instance, a quartic term  $Z_{a_1}^\dagger(\theta_1)Z_{a_2}(\theta_2)Z_{a_3}^\dagger(\theta_3)Z_{a_4}(\theta_4)$ . The projection (38) corresponds to an approximation which drops the higher-order terms of (45) out. To improve the result (41), we need to accurately evaluate the higher-order terms of the expansion (45).

Here, without evaluating the higher-order terms directly, we replace the FZ operators to the fermionic creation and annihilation operators following a rule,

$$Z_a(\theta) \sim \sqrt{\frac{2E(\theta)}{v}} c_a(k), \quad Z_a^\dagger(\theta) \sim \sqrt{\frac{2E(\theta)}{v}} c_a^\dagger(k), \quad (46)$$

with  $k = \Delta_0 \sinh \theta$ . This rule correctly reproduces the anticommutation relations,

$$\begin{aligned} \{c_a(k), c_{a'}(k')\} &= 0, \\ \{c_a^\dagger(k), c_{a'}^\dagger(k')\} &= 0, \\ \{c_a(k), c_{a'}^\dagger(k')\} &= 2\pi \delta_{aa'} \delta(k - k'). \end{aligned}$$

Note that the  $S$  matrix of the  $O(3)$  NLSM (23) approaches the fermionic  $S$  matrix,  $S_{ab}^{cd}(\theta) \rightarrow -\delta_{ad}\delta_{bc}$ , when  $\theta \rightarrow 0$ . Thus, the replacement (46) is valid only around the bottom of the band  $k \sim 0$ . This fermion has a dispersion  $E_a(k) = \sqrt{\Delta_0^2 + k^2} - aH$  ( $a = 0, +, -$ ). This dispersion relation is consistent with the dynamical exponent  $z = 2$  of the free fermion theory (42).

The replacement (46) enables us to compute the normalized shift explicitly.

$$Y_D(T, H) = \frac{3Z_2}{2m(T, H)} \int_{-\infty}^{\infty} \frac{v dk}{4\pi E_0(k)} [2f_0(k) - f_+(k) - f_-(k)] \quad (47)$$

$f_a(k) = (e^{(\sqrt{\Delta_0^2 + k^2} - aH)/T} + 1)^{-1}$  is the Fermi distribution function and  $m(T, H)$  is the magnetization,

$$m(T, H) = \int_{-\infty}^{\infty} \frac{dk}{2\pi} [f_+(k) - f_-(k)]. \quad (48)$$

The analytic result (47) is compared with the QMC results at  $T = 0.1J$  and  $0.2J$  in Fig. 2. The free fermion representation (47) reproduces the minimum of the normalized ESR shift and, furthermore, agrees quantitatively with the QMC data.

## VI. NEAR UPPER CRITICAL FIELD

### A. Effective field theory

The field-induced critical phase ends at the upper critical field  $H = H_{c2}$  where  $H_{c2} = 4J$ . Above the up-

per critical field, the spins are fully polarized, where the gap opens again and the low-energy excitation has a parabolic dispersion. Slightly below the upper critical field ( $H_{c1} \ll H - H_{c1} < 0$ ), almost all spins are polarized. Here we may neglect the  $S_j^z = -1$  component anti-parallel to the magnetic field because it costs huge amounts of energy. Thus, the  $S = 1$  spin is effectively described by an  $S = 1/2$  spin.

$$S_j^z \sim \frac{1}{2}(1 + \sigma_j^z), \quad S_j^\pm \sim \frac{1}{\sqrt{2}}(-1)^j \sigma_j^\pm \quad (49)$$

$(\sigma_j^x, \sigma_j^y, \sigma_j^z)$  is the Pauli matrices and  $\sigma_j^\pm \equiv (\sigma_j^x \pm i\sigma_j^y)/2$ . The unperturbed Hamiltonian (9) is transformed into an effective  $S = 1/2$  XXZ chain.

$$\mathcal{H}^{(0)} \sim \frac{J}{2} \sum_j \left[ -(\sigma_j^x \sigma_{j+1}^x + \sigma_j^y \sigma_{j+1}^y) + \frac{1}{2} \sigma_j^z \sigma_{j+1}^z \right] - \frac{h}{2} \sum_j \sigma_j^z \quad (50)$$

This is effectively written in terms of a free fermion,

$$\mathcal{H}^{(0)} \sim \int_{-\infty}^{\infty} \frac{dk}{2\pi} E(k) c^\dagger(k) c(k), \quad (51)$$

with a quadratic dispersion,

$$E(k) = \frac{k^2}{2m} - \tilde{\mu}. \quad (52)$$

Here  $m = 1/2J$  and  $\tilde{\mu} = H_{c2} - H$  are the mass of the fermion and the chemical potential that the fermion feels. Thus, the effective theories around the upper critical field and the lower critical field are isomorphic, while the mass and the chemical potential of the fermions are different. It should be also noted that the free fermion in each theory represents a different object with respect to the original spin system.

## B. ESR shift

Using the mapping (49), one can represent the normalized shift in the Pauli matrices.

$$Y_D(T, H) = \frac{1}{2} - \frac{1 - \langle \sigma_j^z \rangle_0}{1 + \langle \sigma_j^z \rangle_0} \quad (53)$$

Here the average  $\langle \cdots \rangle_0$  is taken by the Hamiltonian (50) of the effective  $S = 1/2$  XXZ chain. A free fermion theory with the dynamical exponent  $z = 2$  describes the low-energy physics near the upper critical field  $H_{c2}$ . Similarly to eq. (43), the magnetization density  $\langle \sigma_j^z \rangle_0$  is given by the polylogarithm function as

$$\langle \sigma_j^z \rangle_0 = 1 + 2\sqrt{\frac{T}{4\pi J}} \text{Li}_{1/2}(-e^{(H_{c2}-H)/T}). \quad (54)$$

Substituting (54) into (53), we obtain the explicit representation of the normalized shift. We show the normalized ESR shift computed by the free fermion theory in

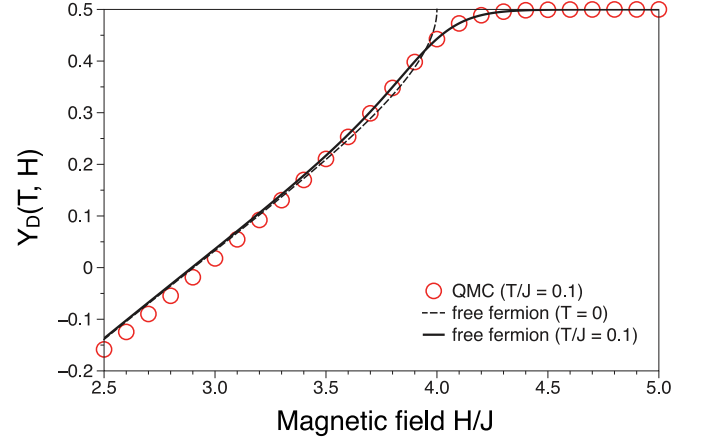


Figure 3. (Color online) The open circles denote the QMC data obtained for 40-site chains at  $T/J = 0.1$ . The solid and dashed curves are derived from the free fermion theory near  $H_{c2}$ . The former is  $T > 0$  data and the latter is  $T = 0$  data. The finite-temperature effect is irrelevant in the lower field range  $H \lesssim 3J$ .

Fig. 3. In order to see the field dependence explicitly, we consider the  $T = 0$  case. The magnetization shows a singular dependence on the magnetic field at  $T = 0$ .

$$\langle \sigma_j^z \rangle_0 = 1 - \frac{2}{\pi} \sqrt{H_{c2} - H} + \mathcal{O}(H_{c2} - H) \quad (55)$$

The normalized shift at  $T = 0$  is shown by the dashed curve in Fig. 3. The free fermion theory (51) appears to work well in the entire region of Fig. 3 in the limit of  $T \rightarrow 0$ . However, the numerical result in Fig. 1 shows a non-negligible temperature dependence for  $H \lesssim 3J$  while the free fermion theory shows little temperature dependence. This corresponds the breakdown of the present picture based on spin flips from the saturated state, in the lower magnetic field.

## VII. NDMAP

We apply our theory of ESR shifts to an  $S = 1$  HAF chain compound  $\text{Ni}(\text{C}_5\text{H}_{14}\text{N}_2)_2\text{N}_3(\text{PF}_6)$  (abbreviated to NDMAP<sup>5,32-34</sup>). There are several  $S = 1$  HAF chain compounds, for instance,  $\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)_2(\text{NO}_2)\text{ClO}_4$  (abbreviated to NENP<sup>35</sup>),  $\text{Ni}(\text{C}_9\text{H}_{24}\text{N}_4)(\text{NO}_2)\text{ClO}_4$  (abbreviated to NTENP<sup>36</sup>) and  $\text{Ni}(\text{C}_5\text{H}_{14}\text{N}_2)_2\text{N}_3(\text{ClO}_4)$  (abbreviated to NDMAZ<sup>37</sup>). Among these  $S = 1$  HAF chain compounds, NDMAP is most suitable to our purpose because NENP has an effective staggered magnetic field  $h \sum_j (-1)^j S_j^x$  and NTENP has a bond alternation  $\delta \sum_j (-1)^j \mathbf{S}_j \cdot \mathbf{S}_{j+1}$ . The staggered magnetization mixes the singlet ground state  $|g\rangle$  and the triplet excited states  $|e\rangle$ :  $\langle e | \sum_j (-1)^j S_j^x | g \rangle \neq 0$ .<sup>12</sup> This mixing changes the selection rule of ESR. Such an interaction is uncovered by our theory. Though the bond alternation does not induce the mixing, when  $H = 0$ , NTENP has a different

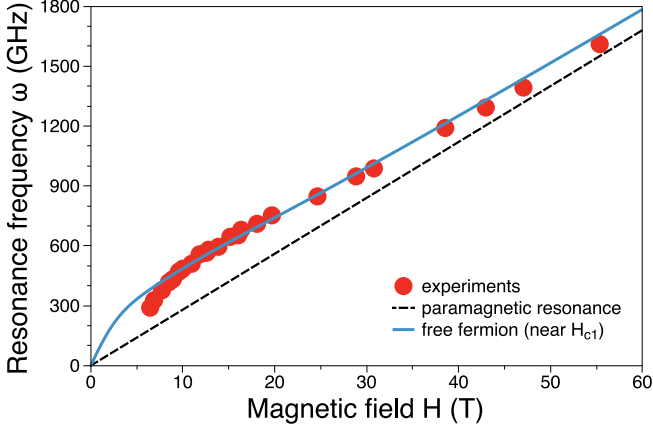


Figure 4. (Color online) Comparison of the free fermion theory (47) with the experimental data on NDMAP at a temperature  $T = 0.05J$ .<sup>5</sup> The solid curve is the free fermion result (47) near  $H_{c1}$  and the solid circles denote the experimental data. We used the parameters  $J = 30.0$  K,  $D/J = 0.25$ , and  $g_e = 2.10$ . The magnetic field is applied along  $c$  axis, which corresponds to  $z_p = 1$ ,  $z_q = z_r = 0$ . The dashed curve is high-temperature paramagnetic resonance frequency  $\omega = g_e\mu_B H$ .

ground state from that of (9).<sup>38</sup> Recently, NTENP has been field theoretically analyzed by using a sine-Gordon model.<sup>39</sup> The compound NDMAZ has very similar crystal structure to NDMAP. In fact, our theory is applicable to NDMAZ. But, NDMAZ has stronger exchange interaction  $J \approx 70.6$  K than NDMAP. The large  $J$  makes the experimental investigation of the field-induced critical phase difficult because of the large  $H_{c1}$ .

Parameters of NDMAP are estimated as follows.<sup>33</sup>

$$J \approx 30.0 \text{ K}, \quad D/J \approx 0.25 \quad (56)$$

The parameter  $E$  is much smaller than  $D$ . Here we consider the field orientation perpendicular to the easy plane,  $(z_p, z_q, z_r) = (1, 0, 0)$ . Thus, the normalized shift is independent of the anisotropy  $E$ .

$$\omega_r = g_e\mu_B H - 2DY_D(T, H) \quad (57)$$

The Landé  $g$  factor is  $g_e = 2.11$ .<sup>5</sup> We substitute the free fermion theory near the lower critical field (47) into (57) and compare it with experimental data by Ref. 5 (Fig. 4). They show semiquantitative agreement. Our theory gives a concrete support to the estimation (56).

Note that there is a zero point  $H = H_0(T)$  where the ESR shift vanishes,

$$Y_D(T, H_0(T)) = 0. \quad (58)$$

In addition to the trivial solution  $H_0 = 0$ , at  $T = 0.1J$ , one can find a zero point  $H_0 \sim 3J$  in Fig. 5. We show several cases  $D/J = 0.1, 0.2$  and  $-0.1$  with the fixed  $J$ . One will be able to experimentally observe the zero point  $H = H_0$  if an  $S = 1$  HAF chain compound with smaller  $J \lesssim 15$  K is found. In general, the zero point  $H_0(T)$

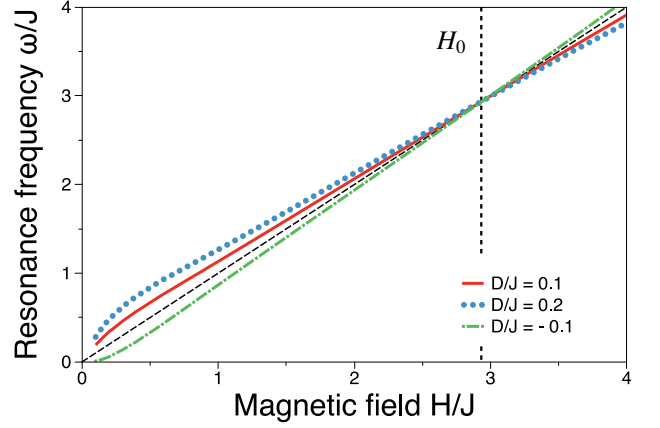


Figure 5. (Color online) QMC data of the resonance frequency (57) at  $T = 0.1J$ . The  $g$  factor is set to  $g_e\mu_B = 1$  for simplicity. The dashed line  $\omega = H$  corresponds to the paramagnetic resonance frequency. Several cases  $D/J = 0.1, 0.2$  and  $-0.1$  are shown. Note that there is a zero point  $H_0 \sim 3J$  where the shift (5) vanishes.

depends on the temperature  $T$ . The non-trivial solution  $H_0(T)$  of (58) exists in a wide range of the temperature because  $Y_D(T, H)$  is negative in  $H \ll H_{c1}$  and positive in  $H \sim H_{c2}$ . In contrast, as we will discuss in the Appendix, for the exchange anisotropy

$$\mathcal{H}' = \sum_j \sum_{a=p,q,r} J'_a S_j^a S_{j+1}^a, \quad (59)$$

we find that the ESR shift in the first order of the anisotropy does not change its sign in the entire range of  $H$ .

By measuring the zero-field excitation gaps, the symmetry of the Hamiltonian (4) can be identified experimentally. Let us suppose that the Hamiltonian has a uniaxial,  $U(1)$  symmetry, broken from the rotational  $SU(2)$  symmetry. This is consistent with a presence of either the single-ion anisotropy (10) or the exchange anisotropy (59). It is usually difficult to distinguish these two kinds of anisotropic interactions because they often lead to qualitatively the same consequences in observables. However, the presence or absence of the zero point  $H_0(T)$  of the shift at  $T \sim H_{c1}$  is a clear signature which distinguishes the two cases. This may provide a new application of ESR, which possesses a high sensitivity to anisotropy unavailable in other types of measurements.

## VIII. SUMMARY

We theoretically investigated the ESR shift caused by a weak single-ion anisotropy in the  $S = 1$  HAF chain. We applied the Kanamori-Tachiki theory (5) to this system, and analyzed it both analytically and numerically. The formula (5) is factorized to  $\delta\omega = f_D(z)Y_D(T, H)$ , which



is composed of the  $T$ ,  $H$ -independent geometrical factor  $f_D(\mathbf{z})$  and the  $T$ ,  $H$ -dependent factor  $Y_D(T, H)$ . In this paper we call  $Y_D(T, H)$  as the normalized ESR shift because the factor  $f_D(\mathbf{z})$  can be regarded as a constant if we fix the field orientation  $\mathbf{z}$ . In contrast, the normalized shift  $Y_D(T, H)$  does not depend on the field orientation. Thus, this factorization allows the general analysis of the ESR shift without specifying the parameters  $D$  and  $E$ .

Quantum Monte Carlo calculations revealed non-monotonic magnetic field dependence of the normalized shift  $Y_D(T, H)$ . The field dependence reflects the finite-temperature crossover of the  $S = 1$  HAF chain, the low-field gapped phase ( $H < H_{c1}$ ), the field-induced critical phase ( $H_{c1} < H < H_{c2}$ ), and the fully polarized phase ( $H_{c2} < H$ ). We employed several effective field theories to explain the field dependence of  $Y_D(T, H)$  in each phase. We used the exact form factors to compute  $Y_D(T, H)$  in the dilute limit  $H, T \rightarrow 0$ . We extend the result in the low-field limit to the finite-field region  $H \sim H_{c1}$  by replacing the FZ operators of the lowest excitations to the fermionic creation and annihilation operators. This replacement is reasonable in  $H \lesssim H_{c1}$  and it works quite well (Fig. 2). Above  $H_{c1}$ , the system is regarded as the TL liquid. Though we did not go into detail of the ESR shift of the TL liquid in the field-induced critical phase, it can be extracted from the analyses around  $H_{c1}$  and  $H_{c2}$ . Near the upper critical field  $H_{c2}$ , the free fermion analysis is again effective (Fig. 3).

Our analysis is found to agree semiquantitatively with the experimental data of NDMAP in Ref. 5. Our theory correctly reproduces the approaching of the resonance frequency to the paramagnetic resonance frequency  $\omega = g_e \mu_B H$ . Furthermore, we predicted the existence of the special value  $H_0$  of the magnetic field where the ESR shift vanishes  $\delta\omega = 0$ . Such a sign change is absent in the case of an exchange anisotropy.

## ACKNOWLEDGMENTS

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## Appendix A: Exchange anisotropy

We have so far considered the single-ion anisotropy as a resource of anisotropic interactions. In this appendix, we treat a perturbative exchange anisotropy instead of the single-ion anisotropy (10). The ESR shift caused by the exchange anisotropy (59) is also factorized just like

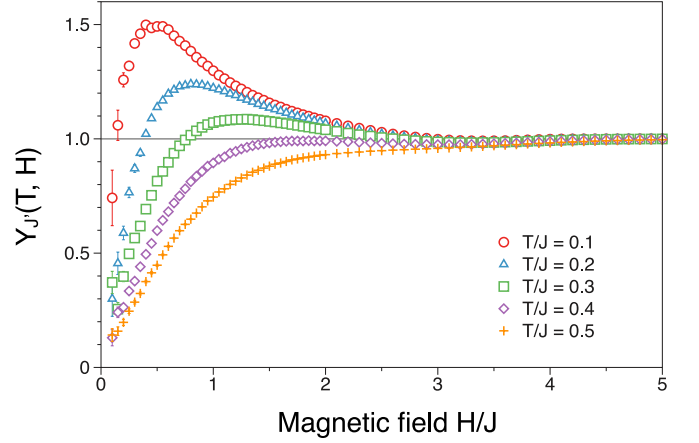


Figure 6. (Color online) Quantum Monte Carlo results of the normalized ESR shift (A3) induced by the exchange anisotropy (59) for temperatures  $T/J = 0.1 - 0.5$ . The system size is  $L = 40$  sites. The maximum around  $H = H_{c1} + T$  is also found in this case. The field dependence of  $Y_{J'}(T, H)$  in a lower field region  $H < J$  at low temperatures  $T < 0.3J$  looks similar to that of  $Y_D(T, H)$  except the overall sign,  $Y_{J'}(T, H) \propto -Y_D(T, H)$ . In a relatively higher temperature  $T > 0.4J$ , the non-monotonic behavior of the normalized shift vanishes.

(11):

$$\delta\omega = f_{J'}(\mathbf{z})Y_{J'}(T, H) \quad (\text{A1})$$

$$f_{J'}(\mathbf{z}) = \sum_{a=p,q,r} J'_a (1 - 3z_a^2) \quad (\text{A2})$$

$$Y_{J'}(T, H) = \frac{1}{2\langle S^z \rangle_0} \sum_j \sum_{a=x,y,z} (3\delta_{az} - 1) \langle S_j^a S_{j+1}^a \rangle_0 \quad (\text{A3})$$

We compute the normalized shift (A3) by QMC in the same manner as (13). Fig. 6 shows QMC results of the normalized shift (A3) at temperatures  $T/J = 0.1 - 0.5$ . The normalized shift  $Y_{J'}(T, H)$  behaves similarly to  $Y_D(T, H)$  in a region where  $T < 0.3J$  and  $H < J$  hold. On the other hand, in a higher field region  $H > J$ , the normalized shift quickly saturates to 1.

First we consider the zero-field case. The effective field theory O(3) NLSM works well at  $H = 0$ . When we move on to the continuum limit, we approximate the product  $S_j^a S_{j+1}^a$  by the composite operator  $[S^a(x)]^2$ ,

$$S_j^a S_{j+1}^a \sim -C[S^a(x)]^2. \quad (\text{A4})$$

The coefficient  $C$  is a non-universal constant. When keeping only the most relevant term  $S^a(x)S^a(x+a_0) \sim -S(S+1)n^a(x)n^a(x+a_0)$ , we may assume  $C > 0$  because the field  $\mathbf{n}(x)$  is smoothly varying on  $x$ . Here  $a_0$  is the lattice spacing and set to unity. The replacement (A4) immediately leads to  $Y_{J'}(T, H) \propto -Y_D(T, H)$  in the infinitesimal field region  $H \ll H_{c1}$ . This relation is consistent with numerical results (Figs. 1 and 6).

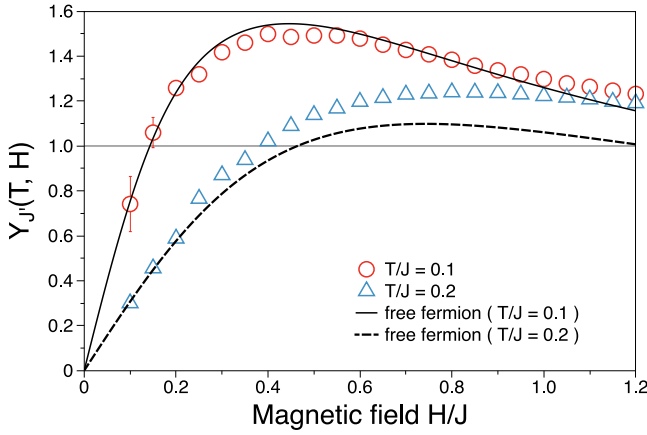


Figure 7. (Color online) Comparisons of QMC and (A5) at  $T/J = 0.1$  and  $0.2$ . The open circles ( $T/J = 0.1$ ) and triangles ( $T/J = 0.2$ ) denote the QMC results. The solid (dashed) curve represents (A5) with  $Z'_2 = 0.41$  at  $T/J = 0.1$  ( $T/J = 0.2$ ).

Next we extend our discussion to the finite field region  $H \sim H_{c1}$  in the exactly same manner with Sec. V. We assume that the replacement (A4) is also valid under not so weak magnetic field  $H \sim H_{c1}$ . Then, the normalized shift  $Y_{J'}(T, H)$  near  $H = H_{c1}$  is given by

$$Y_{J'}(T, H) = -\frac{3Z'_2}{2m(T, H)} \int_{-\infty}^{\infty} \frac{dk}{2\pi} [2f_0(k) - f_+(k) - f_-(k)]. \quad (\text{A5})$$

We determine the phenomenological parameter  $Z'_2$  by fitting (A5) with QMC data at  $T/J = 0.1$ . The fitting leads to  $Z'_2 \approx 0.41$ . Fig. 7 shows the comparison of (A5) and QMC data for  $T/J = 0.1$  and  $0.2$ . The formula (A5) reproduces the QMC data well. But, their agreement rapidly becomes worse as the temperature rises. This discrepancy stems from the saturation value  $Y_{J'}(T, H) \rightarrow 1$  in the limit  $H \rightarrow +\infty$ . While  $Y_D(T, H)$  is negative in the low-field region  $H \ll H_{c1}$ ,  $Y_{J'}(T, H)$  is positive there. Thus, the sign change of the normalized shift does not occur for  $Y_{J'}(T, H)$ . As we have discussed in Sec. VII, this is in contrast to the behavior of  $Y_D(T, H)$ , which universally shows a sign change.

- <sup>1</sup> I. Affleck, Phys. Rev. B **43**, 3215 (1991).
- <sup>2</sup> R. Chitra and T. Giamarchi, Phys. Rev. B **55**, 5816 (1997).
- <sup>3</sup> M. Klanjšek, H. Mayaffre, C. Berthier, M. Horvatić, B. Chiari, O. Piovesana, P. Bouillot, C. Kollath, E. Orignac, R. Citro, and T. Giamarchi, Phys. Rev. Lett. **101**, 137207 (2008).
- <sup>4</sup> E. Čížmár, M. Ozerov, J. Wosnitza, B. Thielemann, K. W. Krämer, C. Rüegg, O. Piovesana, M. Klanjšek, M. Horvatić, C. Berthier, and S. A. Zvyagin, Phys. Rev. B **82**, 054431 (2010).
- <sup>5</sup> T. Kashiwagi, M. Hagiwara, S. Kimura, Z. Honda, H. Miyazaki, I. Harada, and K. Kindo, Phys. Rev. B **79**, 024403 (2009).
- <sup>6</sup> V. N. Glazkov, A. I. Smirnov, A. Zheludev, and B. C. Sales, Phys. Rev. B **82**, 184406 (2010).
- <sup>7</sup> M. Oshikawa and I. Affleck, Phys. Rev. B **65**, 134410 (2002).
- <sup>8</sup> M. Brockmann, F. Göhmann, M. Karbach, A. Klümper, and A. Weiße, Phys. Rev. Lett. **107**, 017202 (2011).
- <sup>9</sup> M. Brockmann, F. Göhmann, M. Karbach, A. Klümper, and A. Weiße, Phys. Rev. B **85**, 134438 (2012).
- <sup>10</sup> Y. Maeda, K. Sakai, and M. Oshikawa, Phys. Rev. Lett. **95**, 037602 (2005).
- <sup>11</sup> I. Affleck, Phys. Rev. B **46**, 9002 (1992).
- <sup>12</sup> T. Sakai and H. Shiba, J. Phys. Soc. Jpn. **63**, 867 (1994).
- <sup>13</sup> S. C. Furuya, T. Suzuki, S. Takayoshi, Y. Maeda, and M. Oshikawa, Phys. Rev. B **84**, 180410 (2011).
- <sup>14</sup> D. Controzzi and G. Mussardo, Phys. Rev. Lett. **92**, 021601 (2004).
- <sup>15</sup> J. Kanamori and M. Tachiki, J. Phys. Soc. Jpn. **17**, 1384 (1962).
- <sup>16</sup> K. Nagata and Y. Tazuke, J. Phys. Soc. Jpn. **32**, 337 (1972).
- <sup>17</sup> K. Nagata, J. Phys. Soc. Jpn. **40**, 1209 (1976).
- <sup>18</sup> Y. Maeda and M. Oshikawa, J. Phys. Soc. Jpn. **74**, 283 (2005).
- <sup>19</sup> S. C. Furuya, P. Bouillot, C. Kollath, M. Oshikawa, and T. Giamarchi, Phys. Rev. Lett. **108**, 037204 (2012).
- <sup>20</sup> S. Todo and K. Kato, Phys. Rev. Lett. **87**, 047203 (2001).
- <sup>21</sup> F. D. M. Haldane, Phys. Rev. Lett. **50**, 1153 (1983).
- <sup>22</sup> F. Haldane, Phys. Lett. A **93**, 464 (1983).
- <sup>23</sup> I. Affleck and F. D. M. Haldane, Phys. Rev. B **36**, 5291 (1987).
- <sup>24</sup> E. S. Sørensen and I. Affleck, Phys. Rev. B **49**, 13235 (1994).
- <sup>25</sup> E. S. Sørensen and I. Affleck, Phys. Rev. B **49**, 15771 (1994).
- <sup>26</sup> J. Balog and P. Weisz, Nucl. Phys. B **778**, 259 (2007).
- <sup>27</sup> E. H. Lieb and W. Liniger, Phys. Rev. **130**, 1605 (1963).
- <sup>28</sup> E. H. Lieb, Phys. Rev. **130**, 1616 (1963).
- <sup>29</sup> I. Affleck, Phys. Rev. B **41**, 6697 (1990).
- <sup>30</sup> Y. Maeda, C. Hotta, and M. Oshikawa, Phys. Rev. Lett. **99**, 057205 (2007).
- <sup>31</sup> R. M. Konik and P. Fendley, Phys. Rev. B **66**, 144416 (2002).
- <sup>32</sup> Z. Honda, H. Asakawa, and K. Katsumata, Phys. Rev. Lett. **81**, 2566 (1998).
- <sup>33</sup> A. Zheludev, Y. Chen, C. L. Broholm, Z. Honda, and K. Katsumata, Phys. Rev. B **63**, 104410 (2001).
- <sup>34</sup> A. Zheludev, Z. Honda, C. L. Broholm, K. Katsumata, S. M. Shapiro, A. Kolezhuk, S. Park, and Y. Qiu, Phys. Rev. B **68**, 134438 (2003).
- <sup>35</sup> J. P. Renard, M. Verdaguer, L. P. Regnault, W. A. C. Erkelens, J. Rossat-Mignod, and W. G. Stirling, Europhys. Lett. **3**, 945 (1987).
- <sup>36</sup> A. Escuer, R. Vicente, and X. Solans, J. Chem. Soc., Dalton Trans., 531 (1997).
- <sup>37</sup> Z. Honda, K. Katsumata, H. A. Katori, K. Yamada, T. Ohishi, T. Manabe, and M. Yamashita,

- J. Phys.: Condens. Matter **9**, L83 (1997).
- <sup>38</sup> T. Suzuki and S.-i. Suga, Phys. Rev. B **72**, 014434 (2005).
- <sup>39</sup> J. Tamaki and M. Oshikawa, Phys. Rev. B **85**, 134431 (2012).